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# CerAMfacturing: development of ceramic and multi material components by additive manufacturing methods for personalized medical products

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Additive manufacturing technologies offer the possibility of tool-free production of components with extremely complex geometry that cannot be attained by any other shaping technique. In our project we are developing a completely new approach for ceramic multi-material additive manufacturing that will allow series production of customized and multifunctional components for manifold applications. In several case studies demonstrators for personalized medical products – micro surgical tools, implants, and remedies – will be manufactured starting with the patient-specific physical dimensions and ending with components validated under practically relevant conditions.

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## Our project

Additive manufacturing (AM) technologies offer the possibility of a tool-free production of components with extremely complex geometry that cannot be attained by any other shaping technique. According to ISO/ASTM, AM is *"the general term for those technologies that based on a geometrical representation creates physical objects by successive addition of material"* [1]. In the plastics industry AM methods are already commercialized to a large extent and the equipment for 3D printing can be even bought for home applications. In the field of metals, more and more materials can be processed as well. For processing ceramic materials, the technical application of AM technologies has been limited so far. However, ceramic materials have been studied in AM processes *ab initio* with the development of the different AM technologies around 25 years [2,3]. All established AM technologies have also been tested for ceramic materials [4–28]. AM technologies can be classified according to the initial state of the used material – powder, liquid and solid [29,30] – or according to the mode of deposition and solidification of the material [31].

For the production of technical ceramic components, AM applies as a shaping process with which only green bodies can be obtained due to the processing properties of ceramic starting materials. A subsequent thermal treatment of the manufactured components by debinding and sintering is required. Accordingly, and besides the technical equipment, these process routes require special know-how, and thus very experienced personnel too. For that reason, the AM of ceramics is very far from becoming home-applicable, yet ceramic components by virtue of their unique material properties are indispensable for consumer goods and medical devices for which AM opens new horizons to realize novel components in so-far 'impossible' geometries.

Within our project 'CerAMfacturing' a completely new approach for ceramic multi-material additive manufacturing is developed that will allow the series production of customized and multifunctional components for manifold applications. In several case studies demonstrators for personalized medical products – micro surgical tools, implants, and remedies – will be manufactured, starting with the patient-specific physical dimensions and ending with components validated under practically relevant conditions. Nine different partners from five European countries are working together on this project that started on the 1 October 2015 and is funded by the EU with more than 5 Mio. € for 3 years.

Future Medicine

To achieve the project goals methods as well as devices have been and will be developed. Especially suspension-based AM methods will be developed and qualified in our project, as this route promises a much better component performance in comparison to powder-based methods. With suspension-based methods, the starting materials are in the form of suspensions, pastes, inks or semi-finished products such as thermoplastic feedstocks, green films or filaments. Since the distribution of the powder particles in a suspension is more homogeneous than in a powder bed, these shaping methods yield higher green densities, which result in sintered components with denser microstructures and lower surface roughness levels. For this purpose, the development work will be focused on:

- Further development of lithography-based ceramic manufacturing (LCM):
  - Increasing the variety of ceramic materials;
  - Increasing the building space for ceramic components.
- Development of fused filament fabrication (FFF), also known as fused deposition modelling (FDM®), for producing large and multi-material ceramic components:
  - Development of particle-filled thermoplastic filaments for FFF;
  - Process development for ceramic and metal-ceramic components manufactured by FFF (printing conditions, debinding and sintering procedure);
  - Further development of FFF-devices to allow the AM of multi-material components.
- Development of thermoplastic 3D printing (T3DP) for producing multi-material ceramic or metal-ceramic components:
  - Development of particle-filled thermoplastic suspensions for T3DP;
  - Process development for ceramic and metal-ceramic components manufactured by T3DP (printing conditions, debinding and sintering procedure);
  - Development of T3DP-devices to allow the AM of multi-material components.

Multi-material applications play a dominant role in this project, as ceramic/ceramic as well as ceramic/metal material combinations are developed. For this, AM methods are to be regarded as qualified shaping methods.

Another approach is to combine AM methods with conventional shaping routes like tape casting or ceramic injection molding. The last-mentioned combination of technologies will allow the individualization of large series production components and the adding of complex structures to standard geometries, respectively.

Characteristic of all these methods used for the production of ceramic-ceramic or metal-ceramic components is the need of post-AM thermal treatment steps such as debinding and sintering, leading to the final properties of the components.

## Co-sintering of multi-material components

In order to obtain a multi-material component, it is a requisite to successfully co-sinter the paired powders of the composite material. As the sintering of the components has to proceed at the same temperature and atmosphere, it is essential that both materials (steel and ceramic) have a comparable sintering temperature. For avoiding critical mechanical stress during cooling, it is also important that the coefficient of thermal expansion of both materials is approximately equal. Concerning the two aforementioned aspects, zirconia and stainless steel are well suited for the composite, which has been verified for example in [32–34].

In the experimental practice of the project CerAMfacturing the particle size of the used zirconia powders was two magnitudes smaller than the particle size of the used stainless steel powders, which results in a higher sinter activity, a higher linear shrinkage and a lower reachable powder content in the feedstocks.

In order to attune the sintering behavior of the two materials to each other, the metallic powder was treated by a high-energy-milling step. Further information about high-energy milling is described in [35,36]. This milling step yields to finer particles and a higher specific surface area [36,37]. Due to this, the sinter activity is increased, which results in a higher sinter density (compared with the starting powder) and accordingly entails a higher shrinkage while the grain size is decreased [36,37]. Furthermore, the high-energy milling process deforms the spherical starting powder to an irregularly and angularly shaped powder. Both, the bulk density of the metal powder and its average particle size decreases. The resulting packing behavior of the treated metal powder is more adapted to the behavior of the ceramic material and their sintering behaviors become comparable [38].

## Used AM techniques & development goals

### Lithography-based ceramic manufacturing (LCM)

This method, developed especially for additive manufacturing of ceramics, operates according to the principle of the so-called digital light processing [9,39,40] and belongs to the vat photopolymerization processes [1]. As with stereolithography, a solidification of a in this case ceramic-particle filled curable monomer suspension is caused by a controlled exposition to light of a defined wavelength leading to a free radical polymerization of the binder system. Via a DLP module, the extensively deposited suspension is selectively irradiated with blue light, whereby all areas get cross-linked on a given plane exposed at the same time. This technology allows the AM of very complex, dense ceramic components with a very fine spatial resolution [41,42].

At the outset of CerAMfacturing only single-material components could be manufactured additively and only very expensive alumina and zirconia suspensions solely distributed by a single company were commercially available. To date, alternative alumina and zirconia suspensions are available as well as a silicon nitride suspension, due to the predicted positive project results. At present the development of a special device is in progress that will allow the AM of multi-material components by means of this AM technology. Nonetheless, the main focus is on the process development to allow for components of a combination of thick dense areas with very fine inner and/or outer structures.

### Fused filament fabrication (FFF)

FFF is based on highly filled thermoplastic mixtures (40–60 vol.-%) with relatively high viscosities (80–300 Pa*s) comparable to feedstocks for ceramic injection molding. These mixtures in the form of filaments are fed to the individual print heads, melted and selectively deposited as strands. Hence, the FFF-technology belongs to the group of material extrusion-based AM processes [1]. The deposited material solidifies on cooling. Through the selective deposition of materials via a number of distinct print heads, diverse material and property gradients of the component can be set. The relatively low attainable resolutions entailed with this method are compensated by a very large build chamber, high productivity and range of materials that can be handled and processed. Due to the high working speeds (up to 50 mm/s) in contrast to most other ceramic AM processes, large components can be realized in a short time. In addition, ceramic fibers can be integrated into the filaments to enable additive manufacturing of ceramic matrix composites (CMCs).

The hardest challenges were the production of the filaments and the development of the thermal processing. Suitable feedstocks need to contain a proportionately high amount of ceramic or metallic particles and have to be convertible into long filaments with a constant diameter. These filaments must be sufficiently strong and elastic so that they can be fed to and passed through the FFF-printing head where they are directly melted. For the fabrication of a high-strength component, in turn, a good interconnection between these filaments within a single layer or among adjacent layers is needed. In addition, subsequent to the AM of the green bodies the defect-free removing of all organic material is needed to allow a fully densification during the final sintering step.

### Thermoplastic 3D printing (T3DP)

Like FFF, T3DP is based on highly filled thermoplastic mixtures (40–67 vol.-%) with a low melting point (80–100°C), except for the fact that their starting viscosities are much lower (0.2–5.0 Pa*s), which allows the deposition of single droplets [43]. T3DP belongs to the group of material jetting AM technologies [1] and bases on a technology and associated production system units that were uniquely developed at Fraunhofer IKTS to overcome a set of major limitations in existing methods. The main focus is on the production of large ceramic green bodies at a higher resolution compared to FFF as well as the functionalization through the use of various materials and a significant increase in build speed compared to LCM. T3DP has the advantage over LCM that it can be used to fabricate multi-component and/or graded parts with almost no restrictions on the selection of materials [38,44–46]. Analogous to the FFF approach, with the T3DP method the material is not deposited over the entire surface, but instead only at the required spots. Printing system-sided, the deposition is realized by means of several heatable dispensing units that can be controlled in all three spatial directions over a fixed platform. The thermoplastic mixture is heated until it reaches a flowable state (80–100°C), is deposited as single droplets at the desired position, and solidifies upon cooling immediately. Since the solidification takes place almost independently of the physical properties of the powders used, even hard metal components can be manufactured [47]. Several supply containers and dispensing units can be used for localized deposition of different materials, including supporting structures, on the same component.

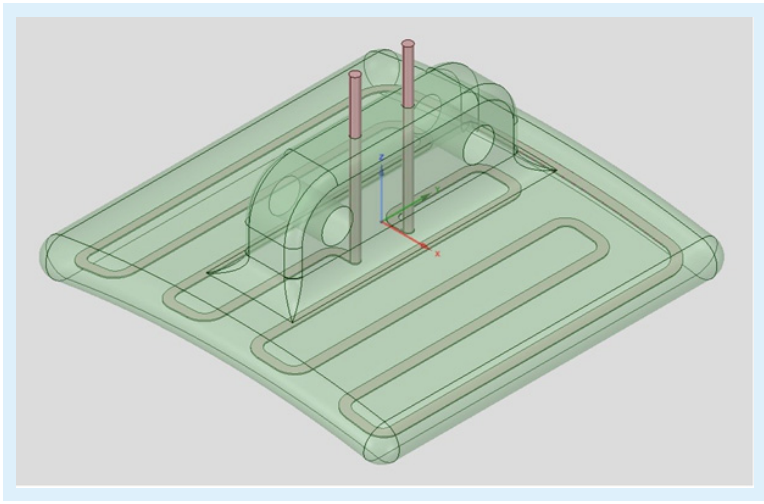

**Figure 1.** CAD-model of ceramic IR heater with electrically conductive structure inside (Ceramicx Ireland LTD).

T3DP pushes back the technological boundaries of AM for ceramics, metals and metal-ceramic components. The deposition of single droplets leads to an attainable resolution in comparison to FFF.

## Case studies

### Customized IR limb heater

The intended application of the IR limb heater is in the treatment of physical ailments where heat is a known or possible remedy. For conditions such as rheumatism, arthritis, post-surgical healing as well as for muscle and fiber damage thermal treatment can be of benefit. The heater will be personalized to the type of the limb or the area of the body to be medically treated, while the overall size of the heater and the shape of the heater will be customized to the requirements of the individual.

Ceramic heaters have been used in the thermal processing of industrial products for over 50 years. The use of a non-contact infrared ceramic heater for localized heating is very common-place in industry. This same principal can be applied to the use of ceramic heaters to locally heat an area as required within the body.

The main challenges are the development of the filaments and the co-sintering of metallic and ceramic powders in large-size components. Figure 1 shows the CAD-model of an IR heater designed by the project partner Ceramicx Ireland LTD.

### Spinal implant & personalized knee partial implant

A herniated or degenerative intervertebral disc can cause nerve root compression and/or spinal cord compression, leading to pain for the patient. In some cases, surgical treatments such as spinal fusion are necessary to improve the quality of life and to prevent from further possible clinical problems. A spinal fusion consists of decompressing two vertebrae after a disc herniation, removal of the damaged disc followed by insertion of a fusion cage between the upper and the lower vertebra to maintain the disc height and lordotic angle.

Chronic knee pain and mobility is a big medical issue affecting an increasingly large number of the adult population. This can be the result of deterioration in the cartilage, which can worsen over time if not treated properly. In some cases, massive bone resection typical for total knee replacement can be avoided. Small osteochondral defects can be treated with partial knee replacements (also called knee partial resurfacing); this is a less invasive solution with advantages such as less bone resection, arthroscopic surgery and less blood loss, therefore shortening the recovery period.

Ceramic 3D printing technologies allow for production of implants with extremely complex geometries that include dense ceramic, textured surfaces and trabecular structures. In general, texturing of the surface has been shown to be advantageous for cell differentiation, bone ingrowth and can enable an increase in implant-to-bone integration.

Due to the complexity of the human knee, the orthopedic community generally agrees that implants customized and adapted to the knee anatomy of each patient can improve the success of the surgery. Every patient has a unique anatomy, size and position of defects. Furthermore, the fixation of the implant itself in the bone is a huge challenge.

**Figure 2.** CAD-model of spinal implant (Ceramtec GmbH).

**Figure 3.** CAD-model of knee partial resurfacing personalized implant (Ceramtec GmbH).

The advantages with additively manufactured spinal implants are:

- The conventional ceramic manufacturing (i.e., green machining by milling and turning) has limitations that make the production of ceramic with textured or trabecular regions too difficult or too expensive. The goal is to quickly manufacture less expensive implants with complex geometries;
- Creating porous rough surfaces that stimulate the bone ingrowth allows for bone integration between the bone and the implant and aids in the primary stability of the implant;
- Creating a lower stable trabecular interconnected structure or avoid the risk of debris release in the body that can lead to implant loosening.

Figures 2 and 3 show two CAD-models designed by our partner Ceramtec GmbH from Germany. These models show the general geometry, but special areas will be filled with complex structures with a very high porosity.

## Individualized gripper for minimally invasive surgery

The goal of the case study development in this project *"individualized gripper minimally invasive surgery"* is to bring focus on the potential of AM of ceramics within the surgical field. For both surgeons, instrument designers and

**Figure 4.** CAD-model of open gripper for minimally invasive surgery (EYE-D Innovation APS; diameter of the shaft is below 6 mm).

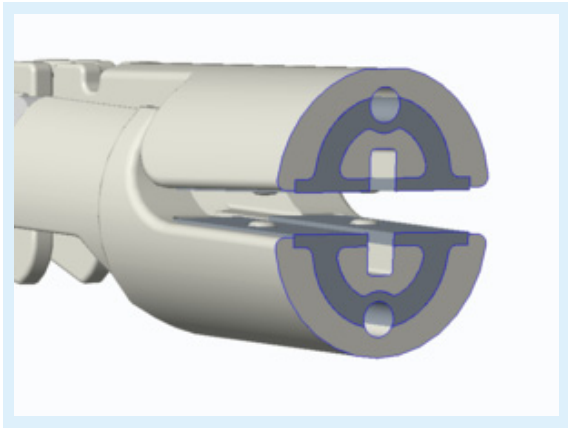

**Figure 5.** Cross section of CAD-model of closed gripper for minimally invasive surgery (EYE-D Innovation APS).

manufacturers, it entails the potential to kick-start a synergetic development of this technology. The demonstrator for this specific case study comprises a gripper and bi-polar ligator used within minimally invasive surgery (MIS). MIS is carried out through small incisions in the body, giving the need for special instruments that can be inserted through the small holes and help to perform the needed functions during surgery. This gripper and ligator can hold, burn and cut tissue and blood vessels by means of integrated gripping jaws, (current-conducting) electrodes, and a knife.

During the planning period, novel AM technologies and a service system could provide the surgeons with custom instruments made specifically for their needs and enhancing their technical skills. In addition, this could possibly lower the costs of production of medical tools and instruments.

Figures 4 and 5 show CAD-models designed by our partner EYE-D Innovation APS from Denmark. The gripper has electrodes to coagulate blood. These will be additively manufactured with zirconia as non-electrically conductive (bright area) and stainless steel as electrically conductive material (dark area). To ensure electrical transmission between cables and electrodes, a channel of conductive material that connects those two has been integrated in the center of the original upper and lower jaw designs.

## Current results

### LCM

Different suspensions were developed that could be used to manufacture additively very fine complex structures as well as dense components. Figures 6 and 7 show two test components manufactured by LCM-technology and with alumina suspensions.

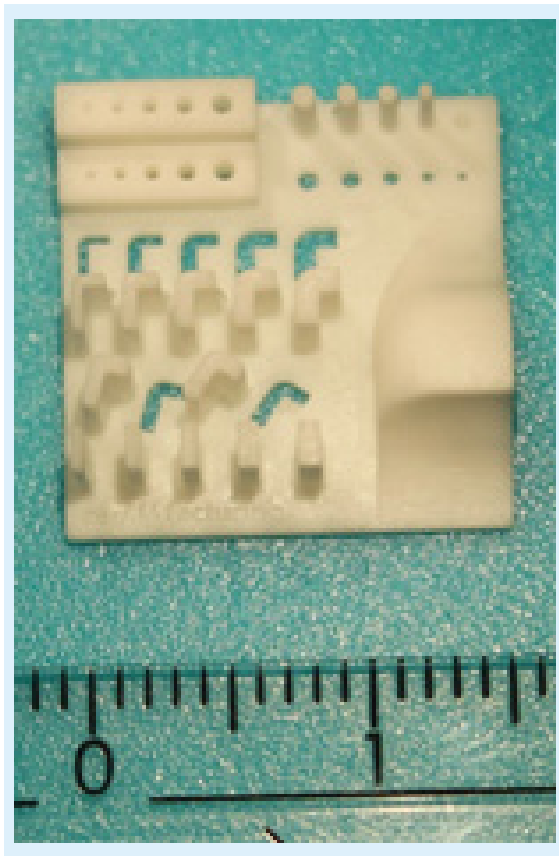


**Figure 6.** alumIna test structure to investigate the tolerances and surface quality, manufactured by LCM (Fraunhofer IKTS).

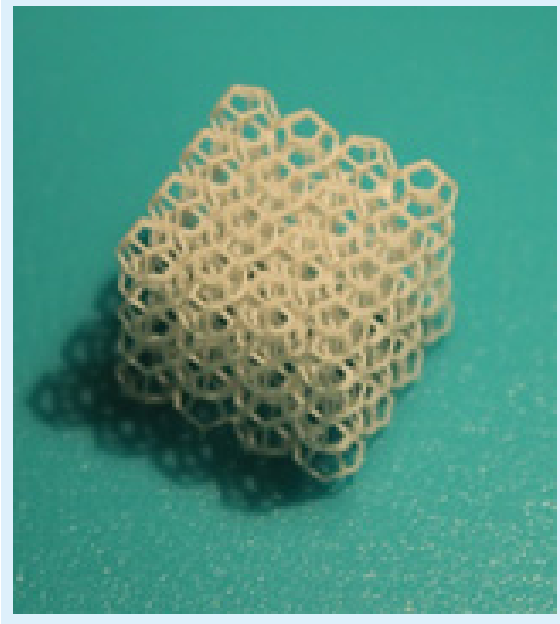

**Figure 7.** Alumina test structure to investigate the resolution, manufactured by LCM (Fraunhofer IKTS). Size: 15 × 15 × 15 $mm^3$.

During our investigations, we noticed the importance of a cleaning step after the printing process. Non-cured suspension has to be removed from the manufactured green body to guarantee the right dimensions and a good surface quality. The results of this investigation were published in [48].

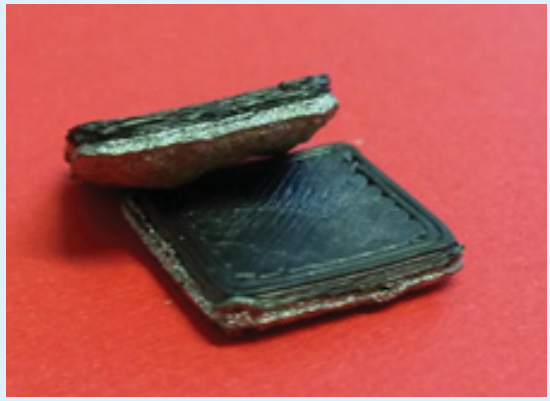

**Figure 8.** Co-sintered metal-ceramic components additively manufactured by FFF (HAGE).

**Figure 9.** Four different dispensing units on the T3DP-device (Fraunhofer IKTS).

Currently the optimization of the curing process is in progress to realize fine and dense geometries in one single component, which normally could not be produced because of the necessary different exposure parameters.

### FFF

Thermoplastic filaments were produced by the Montan University in Leoben (Austria) basing on zirconia and modified stainless steel powder, which could be used by the partner HAGE (Austria) for AM of metal-ceramic components by FFF. Figure 8 shows two metal-ceramic test components ($\sim 15 \times 15 \times 2$ mm$^3$) that were co-sintered at 1365°C for 2 h under hydrogen atmosphere.

### T3DP

Within our project T3DP-suspensions were developed for alumina, zirconia and silicon nitride, as well as thermoplastic suspensions that can be used as supporting material. The T3DP-device in the IKTS-laboratory was enhanced to work in parallel with four different suspensions (Figure 9).

Figure 10 shows a co-sintered test component that was additively manufactured by T3DP and suspensions based on white and black zirconia powders. The manufactured components show a nearly perfect phase separation of both materials, which is very important for further multi-material components with electrically conductive and non-conductive materials in particular.

## Conclusion

The development of the determined suspensions and feedstocks was a success and has nearly been completed for all three different AM techniques. Although the considerable amount of progress that has been made in this field, the device and process development will be further optimized concerning the requirements of the different case studies.

**Figure 10.** Co-sintered multi-material component additively manufactured by T3DP and suspensions based on white and black zirconia powders (Fraunhofer IKTS).

All work packages could be completed in time or are going according to the time schedule and we are feeling optimistic about reaching all project goals, as well as about realizing all demonstrators within the project by overcoming the challenges remained.

## Future perspective

In the next decade AM of ceramics will become more and more state of the art. Complex structures with high surface qualities and high resolutions will address applications in all fields of applications. The portfolio of processible materials will increase significantly and the AM of multi-material components will yield to unprecedented components with unsuspected properties.

### Executive summary

- Additive manufacturing (AM) of technical ceramic components starts with AM of only green bodies.
- A subsequent thermal treatment of the manufactured components by debinding and sintering is required.
- These process routes require special know-how, technical equipment as well as very experienced personnel and AM of ceramics will not become home-applicable.
- Suspension based AM methods promises a much better component performance in comparison to powder-based methods (higher density, better mechanical properties, higher surface quality, etc).
- AM technologies that are based on the selective deposition of material instead of selective solidification are better suited for AM of multi-material components.
- To obtain a defect-free co-sintered multi-material component, it is a requisite to adjust the sintering behavior of the paired powders.
- AM and sintering of defect-free multi-material components is possible.

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